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(54) Title: PROCESS FOR THE PREPARATION OF HYDROXYLATED AROMATIC COMPOUNDS

(57) Abstract: A process is described for preparing hydroxylated aromatic compounds by means of the direct oxidation of an aromatic substrate with hydrogen peroxide in a triphasic reaction system, in the presence of a TS-1 zeolitic catalyst.

5

PROCESS FOR THE PREPARATION OF HYDROXYLATED AROMATIC COM-  
POUNDS

The present invention relates to a process for the  
10 preparation of hydroxylated aromatic compounds by means of  
the direct oxidation of an aromatic substrate with hydrogen  
peroxide.

More specifically, the invention relates to an im-  
proved process for the preparation of hydroxylated aromatic  
15 compounds in which the oxidation reaction with hydrogen  
peroxide is carried out in a triphasic system, in the pres-  
ence of a TS-1 zeolitic catalyst.

Hydroxylated aromatic compounds are used as intermedi-  
ates for the production of phyto-medicines, dyes, pharma-  
20 ceutical compounds, antioxidants, synthetic resins and in-  
secticides.

Among hydroxylated aromatic compounds of major inter-  
est from a commercial point of view, phenol can be men-  
tioned, which is currently industrially produced from cu-  
25 mène.

Various processes for the direct oxidation of aromatic substrates, with hydrogen peroxide in the presence of suitable catalytic systems, are known in the art.

These processes are generally carried out in an organic solvent capable of improving the contact between the  
5 organic substrate and hydrogen peroxide.

The solvents commonly used are selected from alcohols such as methanol, ethanol or isopropyl alcohol, ketones such as acetone, methylethylketone, or acetic acid or acetonitrile as described in U.S. patents 4,396,783, GB  
10 2,116,974.

Improvements in the conversion and selectivities of the above processes can however be obtained by operating in the presence of particular solvents such as, for example,  
15 sulfolane (EP A 919531).

A further process improvement can also be achieved through an activation treatment of the catalyst in an aqueous medium with hydrogen peroxide and in the presence of fluorine ions, as described in European patent application  
20 EP A 958861.

The processes of the known art are generally carried out in a (solid/liquid) biphasic system.

It has now been found that by operating in a triphasic reaction system consisting of solid catalyst/aqueous  
25 phase/organic phase (aromatic compound + solvent) instead

of a biphasic system (solid catalyst/organic phase), it is possible to increase the productivity of oxidation processes of aromatic substrates without jeopardizing the selectivity. Furthermore, by operating in this system, it is possible to significantly reduce the quantity of organic solvent and consequently the dimensions of the recovery section, whose cost greatly influences the overall cost of the process.

An object of the present invention therefore relates to a process for the preparation of hydroxylated aromatic compounds comprising the direct oxidation of an aromatic substrate with hydrogen peroxide, characterized in that the process is carried out in a triphasic reaction system comprising a first liquid phase consisting of the aromatic substrate and an organic solvent, a second liquid phase consisting of water and a solid phase consisting of a catalyst based on titanium silicalite TS-1.

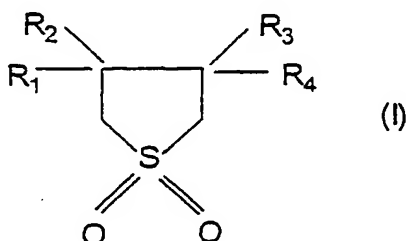
The triphasic reaction system is reached when operating with a controlled quantity of water which is such as to cause the demixing of the liquid phase and prevent the aggregation of the catalyst.

It is convenient to operate with a water concentration ranging from 5 to 60% by weight, preferably using concentrations ranging from 10 to 40%.

The organic solvent can be selected from the solvents

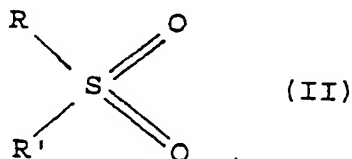
commonly used in oxidation processes described in the known art such as methanol, ethanol, isopropyl alcohol, acetone, methylethylketone, acetic acid or acetonitrile.

The process is preferably carried out in the presence  
5 of solvents having formula (I)



10

wherein:  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , the same or different, are hydrogen atoms or alkyl groups with from 1 to 4 carbon atoms, or among the compounds having general formula (II)



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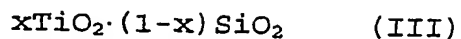
wherein R and R', the same or different, represent an alkyl radical with from 1 to 4 carbon atoms, described in European patent application EP A 919531.

20 Particularly preferred for the purposes of the present invention are compounds having general formula (I) and, among these, sulfolane is preferred.

The solvent is used in quantities ranging from 20 to 80% by weight with respect to the reaction mixture.

25 Quantities ranging from 40 to 60% are preferably used.

The catalysts used in the process of the present invention are selected from those having general formula (III):



5 wherein: x ranges from 0.0001 to 0.04, preferably from 0.02 to 0.03.

The above titanium silicalites can be prepared according to the method described in U.S. patent 4,410,501 in which their structural characteristics are also described.  
10 The titanium silicalites can also be subjected to activation treatment as described in patent EP A 958861.

Titanium silicalites in which part of the titanium is substituted by other metals such as boron, aluminum, iron or gallium, can also be used.

15 These substituted titanium silicalites and the methods for their preparation are described in European patent applications 226,257, 226,258 and 266,825.

The catalyst is generally used in quantities ranging from 2 to 60% by weight with respect to the aromatic substrate.  
20

Quantities of catalyst ranging from 5 to 40% by weight with respect to the aromatic substrate are preferably used.

The hydrogen peroxide is added to the reaction mixture in quantities ranging from 5 to 50% in moles with respect  
25 to the aromatic substrate, preferably from 10 to 30% in

moles.

Solutions of hydrogen peroxide with a concentration ranging from 10 to 60% by weight, preferably from 15 to 60% by weight, are conveniently used. Aromatic substrates which  
5 can be used in the process of the present invention can be selected from benzene, toluene, ethylbenzene, chlorobenzene, anisole, phenol and naphthol.

The aromatic substrate is generally used in quantities ranging from 20 to 80% by weight with respect to the reaction mixture.  
10

Quantities of aromatic substrate ranging from 30 to 60% by weight with respect to the reaction mixture are preferably used.

The oxidation reaction is carried out at temperatures ranging from 50° to 110°C, preferably from 70° to 100°C.  
15

The reaction time necessary for the complete use of the hydrogen peroxide depends on the reaction conditions used.

At the end of the reaction, the reaction products and non-reacted aromatic substrate are recovered by means of the conventional techniques such as fractionated distillation and crystallization.  
20

The process of the present invention can be carried out in reactors of the semi-batch type (with hydrogen peroxide feeding) or of the CSTR type (continuous stirred  
25

batch reactor) with continuous feeding of the hydrogen peroxide and benzene/solvent mixture.

When operating in a continuous process, the aqueous phase (in which the catalyst is selectively distributed),  
5 is kept inside the reactor removing the organic phase to a quiet non-stirred area in which the demixing takes place. In this way, only one phase is obtained at the outlet, containing: an aromatic compound, a solvent, a hydroxy-aromatic compound and the by-products.

10 When operating under the process conditions of the invention, it is also possible to operate at 100°C obtaining an increase in the catalytic activity (TN Ti) without a loss in selectivity, as would normally happen when operating in a double phase.

15 The following examples, whose sole purpose is to describe the present invention in greater detail, should in no way be interpreted as limiting the scope to the invention itself.

The experimentation was carried out using a jacketed,  
20 AISI 316 steel reactor having a capacity of 600 ml, equipped with a mechanical stirrer, feeding lines of the reagents, temperature control and reflux condenser cooled to 0°C.

The solution of H<sub>2</sub>O<sub>2</sub> and, in the case of a continuous  
25 functioning, the benzene/solvent mixture, were fed by means



of piston pumps.

#### EXAMPLE 1

##### Activation of the catalyst

3.0 g (1.43 mmol of Ti) of TS-1 catalyst (EniChem,  
5 Ti = 2.29% by weight) and 0.11 g of  $\text{NH}_4\text{HF}_2$  (average titer  
92.5%) in 35 ml of water, corresponding to a molar ratio  
 $\text{F/Ti} = 2.5$ , are charged into a 100 ml glass flask, equipped  
with a mechanical stirrer, reflux condenser, thermometer  
and oil-circulation thermostat. The aqueous suspension of  
10 the catalyst, maintained under mechanical stirring, is  
heated to 60°C. 1.6 ml of  $\text{H}_2\text{O}_2$  at 30% by weight, equal to a  
molar ratio  $\text{H}_2\text{O}_2/\text{Ti} = 11$ , are subsequently added, and the  
suspension is maintained under stirring at 60°C for 4  
hours. After cooling, the solid is separated from the  
15 mother liquor (pH 4.3) by filtration on a porous septum,  
repeatedly washed with deionized water and finally with  
acetone. The catalyst is then dried under vacuum at 40°C  
for 8 hours and subjected, at a heating rate of 50°C/h, to  
thermal treatment in air at 550°C for 4 hours. Titer of the  
20 activated catalyst = 1.49% of Ti. The dissolved titanium  
corresponds to 35% by weight.

#### EXAMPLE 2

Comparative example: biphasic system (operating under the  
conditions described in patent EP A 958,861)

25 An AISI 316 reactor (volume = 600 ml) is pressurized

with nitrogen at a pressure of 5 atm. 100 g of benzene (1.28 moles), 200 g of sulfolane and 10 g of catalyst activated as described in Example 1 (equal to 3.1 mmol of Ti), are then charged. The liquid phase of the reaction mixture in this case is homogeneous. The temperature of the reactor is brought to 80°C. 14.5 g (128 mmol of H<sub>2</sub>O<sub>2</sub>; H<sub>2</sub>O<sub>2</sub>/benzene = 0.1) of an aqueous solution of H<sub>2</sub>O<sub>2</sub> at 30% w/w) are subsequently added over a period of two hours.

After 15 minutes of conditioning at a constant temperature, under stirring, the reaction mixture is cooled to 20°C and the catalyst is separated by filtration on a porous septum.

The solution is analyzed by means of HPLC revealing the formation of the following products:

15 phenol	7.5 g (79.8 mmol)
hydroquinone	traces (0 mmol)
catechol	traces (0 mmol)

The reaction mixture was then evaporated at reduced pressure obtaining 1.2 g of polyphenol pitches (corresponding to 10.9 mmol of C<sub>6</sub>H<sub>6</sub>O<sub>2</sub> monomer), as boiler residue.

The reaction performances are consequently as follows:

- benzene conversion (C1) = 7.1% (in moles);
- H<sub>2</sub>O<sub>2</sub> conversion (C2) = 99% (in moles);
- selectivity to phenol (S1) = 88% (in moles);
- 25 - selectivity with respect to H<sub>2</sub>O<sub>2</sub> (S2) = 63% (in

moles);

- hourly turnover (TOF) = 11 (phenol moles/Ti moles per hour)
- phenol concentration in the final reaction mixture = 2.38% (by weight).

Operating under these conditions, during the recovery and purification phase of the reaction products, it is necessary to evaporate 41.0 Kg of solvent (sulfolane and non-reacted benzene) per Kg of phenol.

### 10 EXAMPLE 3

#### Comparative example: biphasic system

The same procedure is adopted as described in Example 2, but adding 21.75 (192 mmols of  $\text{H}_2\text{O}_2$ ;  $\text{H}_2\text{O}_2$ /benzene = 0.15) of an aqueous solution of  $\text{H}_2\text{O}_2$  at 30% w/w; in 1 hour at a temperature of 100°C.

The solution is analyzed by means of HPLC revealing the formation of the following products:

phenol	9.64 g (102.6 mmols)
hydroquinone	286 mg (2.6 mmols)
20 catechol	429 mg (3.9 mmols)

The reaction mixture was then evaporated at reduced pressure obtaining 2.46 g of polyphenol pitches (corresponding to 22.4 mmols of  $\text{C}_6\text{H}_6\text{O}_2$  monomer), as boiler residue.

25 The reaction performances are consequently as follows:

- benzene conversion (C1) = 10.3% (in moles);
- H<sub>2</sub>O<sub>2</sub> conversion (C2) = 99% (in moles);
- selectivity to phenol (S1) = 78% (in moles);
- selectivity with respect to H<sub>2</sub>O<sub>2</sub> (S2) = 54% (in moles);
- hourly turnover (TOF) = 33 (phenol moles/Ti moles per hour)
- phenol concentration in the final reaction mixture = 3.00% (by weight).

Operating under these conditions, during the recovery and purification phase of the reaction products, it is necessary to evaporate 32.3 Kg of solvent (sulfolane and non-reacted benzene) per Kg of phenol.

#### EXAMPLE 4

##### Triphasic system under semi-batch conditions

An AISI 316 reactor (volume = 600 ml) is pressurized with nitrogen at a pressure of 5 atm. 100 g of benzene (1.28 moles), 180 g of sulfolane 43 g of water and 10 g of catalyst activated as described in Example 1 (equal to 3.1 mmols of Ti), are then charged. The liquid fraction of the reaction mixture in this case is biphasic. The temperature of the reactor is brought to 80°C. 14.5 g (128 mmols of H<sub>2</sub>O<sub>2</sub>; H<sub>2</sub>O<sub>2</sub>/benzene = 0.1) of an aqueous solution of H<sub>2</sub>O<sub>2</sub> at 30% w/w) are subsequently added over a period of two hours.

The reaction mixture is then cooled to 20°C and the

catalyst is separated by filtration on a porous septum.

The liquid phase is analyzed by means of HPLC revealing the formation of the following products:

	phenol	8.7 g (92.4 mmoles)
5	hydroquinone	264 mg (2.4 mmoles)
	catechol	385 mg (3.5 mmoles)

The reaction mixture was then evaporated at reduced pressure obtaining only traces of polyphenol pitches as boiler residue.

10 The reaction performances are consequently as follows:

- benzene conversion (C1) = 7.7% (in moles);
- H<sub>2</sub>O<sub>2</sub> conversion (C2) = 95% (in moles);
- selectivity to phenol (S1) = 94% (in moles);
- selectivity with respect to H<sub>2</sub>O<sub>2</sub> (S2) = 76% (in  
15 moles);
- hourly turnover (TOF) = 15 (phenol moles/Ti moles per hour)
- phenol concentration in the organic phase = 3.11% (by weight).

20 Operating under these conditions, during the recovery and purification phase of the reaction products, it is necessary to evaporate 31.2 Kg of solvent (sulfolane and non-reacted benzene) per Kg of phenol.

#### EXAMPLE 5

25 Triphasic system under semi-batch conditions

The same procedure is adopted as in Example 4, but adding 21.75 (192 mmol of  $\text{H}_2\text{O}_2$ ;  $\text{H}_2\text{O}_2/\text{benzene} = 0.15$ ) of an aqueous solution of  $\text{H}_2\text{O}_2$  at 30% w/w, in 2 hours at a temperature of  $80^\circ\text{C}$ .

5        The solution is analyzed by means of HPLC revealing the formation of the following products:

phenol	12.7 g (135.0 mmol)
hydroquinone	660 mg (6.0 mmol)
catechol	990 mg (9.0 mmol)

10       The reaction mixture was then evaporated at reduced pressure obtaining only traces of polyphenol pitches as boiler residue.

The reaction performances are consequently as follows:

- benzene conversion ( $\text{C}_1$ ) = 11.7% (in moles);
- 15 -  $\text{H}_2\text{O}_2$  conversion ( $\text{C}_2$ ) = 95% (in moles);
- selectivity to phenol ( $\text{S}_1$ ) = 90% (in moles);
- selectivity with respect to  $\text{H}_2\text{O}_2$  ( $\text{S}_2$ ) = 74% (in moles);
- hourly turnover (TOF) = 22 (phenol moles/Ti moles per  
20 hour)
- phenol concentration in the final reaction mixture = 4.53% (by weight).

Operating under these conditions, during the recovery and purification phase of the reaction products, it is necessary to evaporate 21.1 Kg of solvent (sulfolane and non-  
25

reacted benzene) per Kg of phenol.

#### EXAMPLE 6

##### Triphasic system under semi-batch conditions

The same procedure is adopted as in Example 4, but  
5 adding 21.75 (192 mmol of  $\text{H}_2\text{O}_2$ ;  $\text{H}_2\text{O}_2/\text{benzene} = 0.15$ ) of an aqueous solution of  $\text{H}_2\text{O}_2$  at 30% w/w, in 1 hour at a temperature of 100°C.

The solution is analyzed by means of HPLC revealing the formation of the following products:

10	phenol	13.3 g (141.1 mmol)
	hydroquinone	693 mg (6.3 mmol)
	catechol	1034 mg (9.4 mmol)

The reaction mixture was then evaporated at reduced pressure obtaining only traces of polyphenol pitches as  
15 boiler residue.

The reaction performances are consequently as follows:

- benzene conversion (C1) = 12.2% (in moles);
- $\text{H}_2\text{O}_2$  conversion (C2) = 98% (in moles);
- selectivity to phenol (S1) = 90% (in moles);
- 20 - selectivity with respect to  $\text{H}_2\text{O}_2$  (S2) = 75% (in moles);
- hourly turnover (TOF) = 46 (phenol moles/Ti moles per hour)
- phenol concentration in the final reaction mixture =  
25 4.75% (by weight).

Operating under these conditions, during the recovery and purification phase of the reaction products, it is necessary to evaporate 20.1 Kg of solvent (sulfolane and non-reacted benzene) per Kg of phenol.

5        A comparison between the results obtained in the biphasic and triphasic system, operating under semi-batch conditions, is provided in Table 1.

10

15

20



Table 1

Example nr.	Benzene % w/w (a)	Sulfolane % w/w (a)	H <sub>2</sub> O % w/w (a)	H <sub>2</sub> O <sub>2</sub> (b)	T °C	Conv. % benzene (C1)	Selec. % benzene (S1)	Selec. % H <sub>2</sub> O <sub>2</sub> (S2)	TOF (c)	Conc. % phenol (d)	Kg solv. Kg <sub>phenol</sub> (e)
2	33	67	0	10	80	7.1	88	63	11	2.38	41.0
3	33	67	0	15	100	10.3	78	54	33	3.00	32.3
4	31	56	13	10	80	7.7	94	76	15	3.11	31.2
5	31	56	13	15	80	11.7	90	74	22	4.53	21.1
6	31	56	13	15	100	12.2	90	75	46	4.75	20.1

(a) weight percentage with respect to the reaction mixture

(b) H<sub>2</sub>O<sub>2</sub> moles/benzene moles

(c) hourly turnover of titanium (phenol moles/titanium moles per hour)

(d) wt % concentration of phenol in the final reaction mixture (in the triphasic system only the organic phase was considered)

(e) Kg of solvent to be evaporated in the recovery phase per 1 Kg of phenol produced.

EXAMPLE 7Triphasic system under CSTR conditions (process in continuous)

An AISI 316 reactor (volume = 600 ml) was equipped  
5 with a column (material: AISI 316, internal diameter: 1  
cm), fixed at the head, and immersed in the reaction mixture. A non-stirred zone is created inside the column, in  
which it is possible to selectively remove the organic  
phase (light phase).

10 The reactor is pressurized with nitrogen at a pressure  
of 5 atm. 100 g of benzene (1.28 moles), 150 g of sulfolane  
150 g of water and 50 g of catalyst activated as described  
in Example 1 (equal to 15.5 mmoles of Ti), are then  
charged. The liquid fraction of the reaction mixture in  
15 this case is biphasic. The temperature of the reactor is  
brought to 100°C.

A mixture of benzene (38.3% by weight), sulfolane  
(57.5% by weight and H<sub>2</sub>O<sub>2</sub> (solution at 60% w/w) is then  
fed in continuous (flow: 500 g/hour).

20 766 g of benzene (9.82 moles) and 84 g of H<sub>2</sub>O<sub>2</sub> (60%  
w/w; 1.48 moles), corresponding to a H<sub>2</sub>O<sub>2</sub>/benzene ratio =  
0.15, are then fed over a period of 4 hours.

The level inside the reactor is kept constant by re-  
moving the organic phase which is separated in the quiet  
25 zone inside the tube immersed in the reaction medium.

The organic phase is subsequently analyzed by means of HPLC revealing the formation of the following products:

	phenol	88.5 g (942 mmols)
	hydroquinone	6.16 g (56 mmols)
5	catechol	9.24 mg (84 mmols)

The reaction mixture was then evaporated at reduced pressure obtaining only traces of polyphenol pitches as boiler residue.

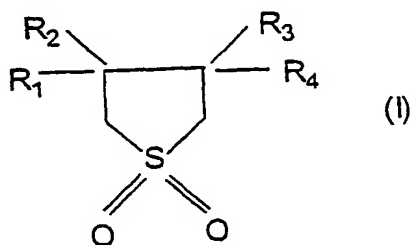
The reaction performances are consequently as follows:

- 10 - benzene conversion (C1) = 11.0% (in moles);
- H<sub>2</sub>O<sub>2</sub> conversion (C2) = 95% (in moles);
- selectivity to phenol (S1) = 87% (in moles);
- selectivity with respect to H<sub>2</sub>O<sub>2</sub> (S2) = 67% (in moles);
- 15 - hourly turnover (TOF) = 30 (phenol moles/Ti moles per hour)
- phenol concentration in the organic phase = 4.43% (by weight).

Operating under these conditions, during the recovery  
20 and purification phase of the reaction products, it is necessary to evaporate 21.6 Kg of solvent (sulfolane and non-reacted benzene) per Kg of phenol.

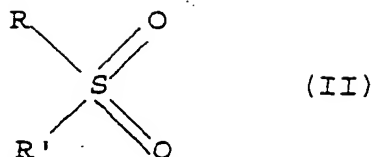
CLAIMS

1. A process for the preparation of hydroxylated aromatic compounds comprising the direct oxidation of an aromatic substrate with hydrogen peroxide, characterized in that the process is carried out in a triphasic reaction system comprising a first liquid phase consisting of the aromatic substrate and an organic solvent, a second liquid phase consisting of water and a solid phase consisting of a catalyst based on titanium silicate TS-1.
2. The process according to claim 1, wherein the quantity of water in the reaction system ranges from 5 to 60% by weight.
3. The process according to claim 2, wherein the quantity of water ranges from 10 to 40%
4. The process according to claim 1, wherein the organic solvent is selected from solvents having formula (I)



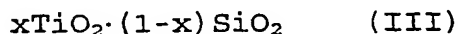
wherein: R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>, the same or different, are hydrogen atoms or alkyl groups with from 1 to 4 carbon atoms, or among the compounds having general formula

(II)



5        wherein R and R', the same or different, represent an alkyl radical with from 1 to 4 carbon atoms.

5.        The process according to claim 4, wherein the organic solvent is selected from the compounds having general formula (I).
- 10    6.        The process according to claim 5, wherein the organic solvent is sulfolane.
7.        The process according to claim 1, wherein the organic solvent is used in quantities ranging from 20 to 80% by weight with respect to the reaction mixture.
- 15    8.        The process according to claim 7, wherein the organic solvent is used in quantities ranging from 40 to 60%.
9.        The process according to claim 1, wherein the catalyst is selected from those having general formula (III):



20        wherein: x ranges from 0.0001 to 0.04, preferably from 0.02 to 0.03.

10.        The process according to claim 9, wherein the catalyst is used in quantities ranging from 2 to 60% with respect to the aromatic substrate.
- 25    11.        The process according to claim 10, wherein the cata-

lyst is used in quantities ranging from 5 to 40% with respect to the aromatic substrate.

12. The process according to claim 9, wherein the catalyst is subjected to activation treatment.

5 13. The process according to claim 1, wherein the hydrogen peroxide is added to the reaction mixture in quantities ranging from 5 to 50% in moles with respect to the aromatic substrate.

10 14. The process according to claim 13, wherein the hydrogen peroxide is added to the reaction mixture in quantities ranging from 10 to 30% in moles with respect to the aromatic substrate.

15 15. The process according to claim 1, wherein the hydrogen peroxide is used in a solution at a concentration ranging from 10 to 60%.

16. The process according to claim 15, wherein the hydrogen peroxide is used in a solution at a concentration ranging from 15 to 60% by weight.

20 17. The process according to claim 1, wherein the aromatic substrate is selected from benzene, toluene, ethylbenzene, chlorobenzene, anisole, phenol and naphthol.

18. The process according to claim 17, wherein the aromatic substrate is benzene.

25 19. The process according to claim 1, wherein the aromatic substrate is used in quantities ranging from 20 to 80%

by weight with respect to the reaction mixture.

20. The process according to claim 19, wherein the aromatic substrate is used in quantities ranging from 30 to 60% by weight with respect to the reaction mixture.

5 21. The process according to claim 1, wherein the oxidation reaction is carried out at temperatures ranging from 50° to 110°C.

22. The process according to claim 21, wherein the oxidation reaction is carried out at temperatures ranging  
10 from 70° to 100°C.

23. The process according to claim 1, wherein the oxidation reaction is carried out in reactors of the semi-batch type, with feeding of hydrogen peroxide, or of the CSTR type (continuous stirred batch reactor) with  
15 continuous feeding of hydrogen peroxide and of the aromatic substrate/solvent mixture.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12169

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C37/60 C07C39/04 C07C39/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 919 531 A (ENICHEM SPA) 2 June 1999 (1999-06-02) the whole document	1-23
X	EP 0 958 861 A (ENI SPA ; ENICHEM SPA (IT)) 24 November 1999 (1999-11-24) *abstract; pages 2-4; examples 17-47 and the claims	1-23
X	US 5 811 599 A (ALIVE KESHA VARAJA ET AL) 22 September 1998 (1998-09-22) *abstract; columns 1-3; column 5, lines 29-51; examples 2-12 and the claims*	1-23
X	EP 0 791 558 A (ENICHEM SPA) 27 August 1997 (1997-08-27) *abstract; examples 24-28 and the claims*	1-3, 7-13, 17-23
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

24 January 2003

Date of mailing of the international search report

05/02/2003

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12169

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 894 783 A (ENICHEM SPA) 3 February 1999 (1999-02-03) *abstract; claims 1 and 24-28* -----	1-23
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/12169

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0919531	A	02-06-1999	IT MI972629 A1 EP 0919531 A1 JP 11240847 A RU 2185368 C2 TW 466230 B US 6133487 A	27-05-1999 02-06-1999 07-09-1999 20-07-2002 01-12-2001 17-10-2000
EP 0958861	A	24-11-1999	IT MI981087 A1 IT MI982712 A1 DE 69901654 D1 EP 0958861 A1 JP 2000202305 A RU 2159675 C1 US 6288004 B1	19-11-1999 19-06-2000 11-07-2002 24-11-1999 25-07-2000 27-11-2000 11-09-2001
US 5811599	A	22-09-1998	NONE	
EP 0791558	A	27-08-1997	IT MI960330 A1 IT MI961836 A1 AT 210077 T CZ 9700543 A3 DE 69708723 D1 DE 69708723 T2 DK 791558 T3 EP 0791558 A1 ES 2167626 T3 JP 10001309 A PL 318605 A1 PT 791558 T SI 791558 T1 SK 23597 A3 TW 403722 B US 5965476 A	22-08-1997 06-03-1998 15-12-2001 17-09-1997 17-01-2002 14-08-2002 18-03-2002 27-08-1997 16-05-2002 06-01-1998 01-09-1997 31-05-2002 30-04-2002 04-03-1998 01-09-2000 12-10-1999
EP 0894783	A	03-02-1999	IT MI971806 A1 EP 0894783 A1	29-01-1999 03-02-1999